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Simultaneous Measurements of Stress and Infrared Dichroism of Polychloroprene

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In order to obtain informations on the molecular nature and mechanism of rheological processes on polymers, simultaneous measurements of stress and infrared dichroism were made of polychloroprene films (Neoprene Type AC) during the course of continuous elongation at a constant rate and of stress relaxation. The time dependence of the infrared dichroism was obtained by measuring the intensity change at fixed wavenumbers of absorption band maxima on the differential polarized infrared spectra described in a previous paper¹⁾. Both the degree of crystallinity of sample films and the orientation function of the transition moment with respect to the stretching direction were calculated from the results of the infrared dichroic measurements using a model of uniaxial orientation, which was confirmed to be the case by x-ray diffraction and birefringence measurements.

In the continuous elongation experiments, it was found that the orientation functions for crystalline-sensitive bands showed maxima at 25% elongation and then decreased rapidly changing their signs from positive to negative. There also appeared at 25% elongation the yield point in the stress-strain curve and the beginning of sharp decrease of crystallinity. These facts were interpreted in terms of the orientation of the crystalline phase followed by the degradation of crystallites and drawing out of the molecular chain from the crystallites. In the stress relaxation experiments, moderate changes in the orientation functions were found for various characteristic absorption bands. Little difference was observed between changes in the orientation functions for the amorphous and crystalline-sensitive bands. This makes a contrast with the previous results for vulcanized natural rubber¹⁾, where the orientation of the crystalline phase was completed almost immediately after elongation, while in the amorphous phase the molecular chains were oriented gradually during the course of stress relaxation.

INTRODUCTION

In preceding papers, we have proposed a method for simultaneous measurements of stress and infrared dichroism of polymer films using a double beam infrared spectrometer¹⁾ and applied it to studies of mechanical behaviour of various polymers, such as natural rubber¹⁾, polyethylene²⁾, and polyvinylchloride containing small amounts of diethyl phthalate or dioctyl phthalate as plasticizer³⁾.

In the present work, the same method was used for the studies of continuous elongation and stress relaxation of polychloroprene films at room temperature. The result obtained in the continuous elongation experiments was discussed in a point of view of orientations of molecules and crystallites in the sample films

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and that obtained in the stress relaxation experiments was compared with the results of the same type of study for natural rubber¹⁾.

EXPERIMENTAL

Polychloroprene sample used is Neoprene Type AC, from E. I. du Pont de Nemours and Company, Inc., having the density of 1.23 and refractive index of 1.554. It had been shown⁴⁾ that it consists predominantly of a linear sequence of the *trans*-2-chloro-2-butenylene units which result from 1,4-polymerization of chloroprene. Other structures which are slightly present include those resulting from *cis*-1,4-polymerization, from 1,2-polymerization, and from 3,4-polymerization. It has also been said that this sample crystallizes in a few hours at room temperature⁵⁾ and the crystal melts at about 50°C⁶⁾.

The films were prepared by casting from benzene solution at room temperature, the film thickness being about 30 μ . The degree of crystallinity of the samples thus obtained was about 25 % as determined by means of infrared intensity measurements⁶⁾. They were cut into rectangular pieces 28 mm wide 52 mm long, and held between two clamps of a stretching device with margin of 6 mm each. In the stress relaxation experiments, the films were rapidly stretched up to 400 % elongation in the same way as in the case of natural rubber¹⁾. In the continuous elongation experiments, on the other hand, they were stretched at the constant rate of 25 %/min using a system of electric motor and gearbox, which was connected to the stretching device through a steel wire. All the experiments were carried out in a room of constant temperature ($22 \pm 0.5^\circ\text{C}$) and constant humidity ($45 \pm 1\%$). Using both the x-ray diffraction and birefringence measurements, it is confirmed that the films can virtually be considered to have uniaxial orientation.

The apparatus for simultaneous measurements of stress and infrared dichroism is the same as that shown in the previous paper¹⁾, except for the direction of the polarization planes of two polarizers. In the present study, one polarizer in the sample beam and the other in the reference beam were placed so that the beams emerging from them were polarized to have the electric vectors perpendicular and parallel, respectively, to the stretching direction of the sample. This orientation of the two polarizers is just the opposite of that in the previous case¹⁾. Thus, when the movement of a pen on the spectrometer is recorded as a function of wavenumber by this method, one can have a differential polarized spectrum described in the previous paper¹⁾. In this case, parallel bands in the ordinary polarized spectrum appear as upward peaks in the differential polarized spectrum, whereas perpendicular bands as downward peaks. On the other hand, setting the spectrometer at one of the wavenumbers of the absorption band maxima, one can continuously record the change in its dichroism during mechanical treatments which give rise to the molecular orientation in the sample.

ORIENTATION FUNCTION

In order to characterize the orientation of polymer chains and crystallites in

the stretched sample, the orientation function F of a transition moment with respect to the stretching direction, defined as⁷⁾

$$F = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = \frac{1}{A_{\parallel} + 2A_{\perp}} \log T \quad (1)$$

was used under the confirmed assumption of uniaxial orientation. Here A_{\parallel} and A_{\perp} are the absorbances of the sample for the polarized radiations with the electric vectors parallel and perpendicular, respectively, to the stretching direction. T is the quantity recorded on the spectrometer when the sample and two polarizers are arranged as is shown in Fig. 2 of the reference (1) with the slight alteration mentioned above, and is expressed by

$$T = \frac{I_s}{I_R} = 10^{(A_{\parallel} - A_{\perp})} \quad (2)$$

where I_s and I_R are the intensities of the sample beam and reference beam, respectively, transmitted through the sample.

One-third of the denominator in the right-hand side of eq.(1), that is

$$\frac{1}{3} (A_{\parallel} + 2A_{\perp}) \equiv A \quad (3)$$

gives the absorbance which would have been obtained if orientation were absent⁸⁾. It is therefore independent of the state of orientation and is proportional to the amount of absorbing centers in the oriented sample. Thus it is possible to know the change in crystallinity of the sample during mechanical treatments by measuring the change in $(A_{\parallel} + 2A_{\perp})/d$ or $(\log T + 3A_{\perp})/d$ for crystalline-sensitive bands. Here d is the film thickness. For the crystalline-insensitive band, the change in the A value can be used as a measure of the change in film thickness.

When the axis of the polymer chain forms an angle α with the stretching direction, the orientation function F for a polymer band can be expressed by

$$F = \frac{1}{2} (3 \overline{\cos^2 \alpha} - 1) \cdot \frac{1}{2} (3 \overline{\cos^2 \theta} - 1) \quad (4)$$

where θ is an angle between the chain axis and the transition moment of the band. In the case of the crystalline orientation, on the other hand, the orientation function F_a , F_b , and F_c of three crystal axes a , b , and c can be given by

$$F_a = \frac{1}{2} (3 \overline{\cos^2 \gamma} - 1) \quad (5)$$

$$F_b = \frac{1}{2} (3 \overline{\cos^2 \delta} - 1) \quad (6)$$

and

$$F_c = \frac{1}{2} (3 \overline{\cos^2 \varepsilon} - 1) \quad (7)$$

Here, γ , δ , and ε represent the angles between the stretching direction and the crystal axes, a , b , and c , respectively.

In the present work, the imperfection of polarization in the transmitted radiation of polarizer⁹⁾ was evaluated to be 0.06 for our polarizers made of six silver

chloride plates, and the correction for this imperfection was carried out in the calculation of A_{\parallel} , A_{\perp} , and T . No correction was necessary for the polarization characteristics of the monochromator or the prism polarization, because the stretching direction of the sample and the two polarizers were tilted by 45° with respect to the entrance slit of the monochromator as was described in the previous report¹⁾.

RESULTS AND DISCUSSION

1. Ordinary polarized and differential polarized infrared spectra and band assignments

Fig. 1A shows the ordinary polarized infrared absorption spectra of the polychloroprene film stretched by 300 %. The solid and broken lines represent the absorption curves obtained for the polarized radiations with the electric vectors perpendicular and parallel, respectively, to the stretching direction. Fig. 1B is the differential polarized infrared spectrum of the same film. The broken line in this figure gives the same type of spectrum obtained for unstretched sample, giving nearly a straight line. It is apparent from Figs. 1A and 1B that infrared dichroism can be observed much more definitely in the differential polarized spectrum than in the ordinary polarized spectra.

Infrared absorption spectra of amorphous and crystalline Neoprene have been studied by Mochel and Hall¹⁰⁾, who have made tentative assignments of the major

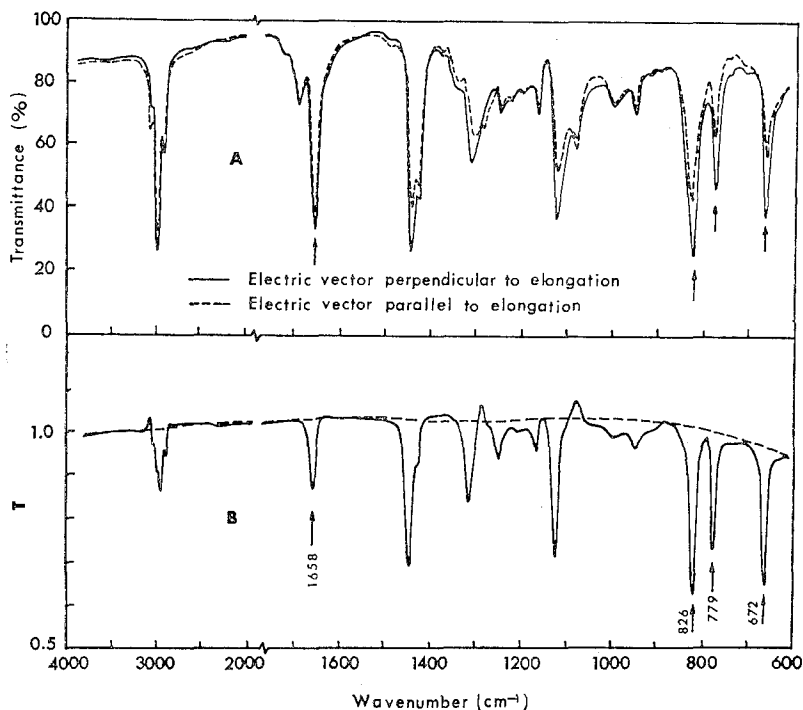


Fig. 1. Ordinary polarized (A) and differential polarized (B) infrared spectra of elongated polychloroprene film.

bands. It was found that the absorption bands observed at 672, 779, and 955 cm^{-1} in Figs. 1A and 1B were absent in the spectra of amorphous sample, but appeared with crystallization, and then greatly enhanced with increasing crystallinity. These absorption bands therefore definitely appear to be associated with crystallization in the sample. It was also found in the present study that a broad band was observed at about 820 cm^{-1} in the amorphous sample and narrowed with crystallization, shifting its maximum to 826 cm^{-1} . This fact suggests that there occurs the overlap of the amorphous and crystalline-sensitive bands in this region. Crystallization caused less pronounced spectral change in a group of the absorption bands between 1500 and 1000 cm^{-1} . Little or no effect of crystallization was found for the band at 1658 cm^{-1} . Almost all the absorption bands mentioned above gave rise to strong perpendicular dichroism when the sample was highly stretched.

Four absorption bands at 672, 779, 826, and 1658 cm^{-1} were used for evaluating the orientation of crystallites and molecular chains. The characteristic behavior of these bands on crystallization are summarized in Table 1, together with their tentative assignments determined by us referring to the results of Mochel and Hall⁽¹⁰⁾.

Table 1. Infrared absorption bands (used in this study) of polychloroprene.

Wavenumber (cm^{-1})	Dichroism in highly stretched sample	Assignment (Symmetry species)	Effect of crystallization
1658	\perp	C=C stretching	No change
826	\perp	=C—H out-of-plane deformation	Narrows with crystallization
779	\perp	CH ₂ rocking (B_2 or B_3)	Appears with crystallization
672	\perp	C—Cl stretching (B_2 or B_3)	Appears with crystallization

According to the x-ray diffraction studies by Bunn⁽¹¹⁾, polychloroprene crystallizes in the orthorhombic system, Space Group D_2^4 , with $a=8.84\text{\AA}$, $b=10.24\text{\AA}$, and $c=4.79\text{\AA}$. Four long chain molecules pass through the unit cell parallel to the c -axis. In this system, the infrared-active vibrations are divided into three symmetry species B_1 , B_2 , and B_3 which have the transition moments parallel to the crystal axes c , b , and a , respectively. Since the C—Cl bond and a line connecting two hydrogen atoms in CH₂ group are nearly parallel to the ab -plane⁽¹¹⁾, it is quite possible that the C—Cl stretching and CH₂ rocking vibrations belonging to the B_2 or B_3 species are much stronger than those belonging to the B_1 species. Therefore, the crystalline-sensitive bands observed at 672 and 779 cm^{-1} can virtually be attributed to the C—Cl stretching and CH₂ rocking vibrations, respectively, of the B_2 or B_3 species. Thus, the transition moments of these bands can be thought to be parallel to the ab -plane, then perpendicular to the chain axis in the crystal.

2. Continuous elongation at constant rate

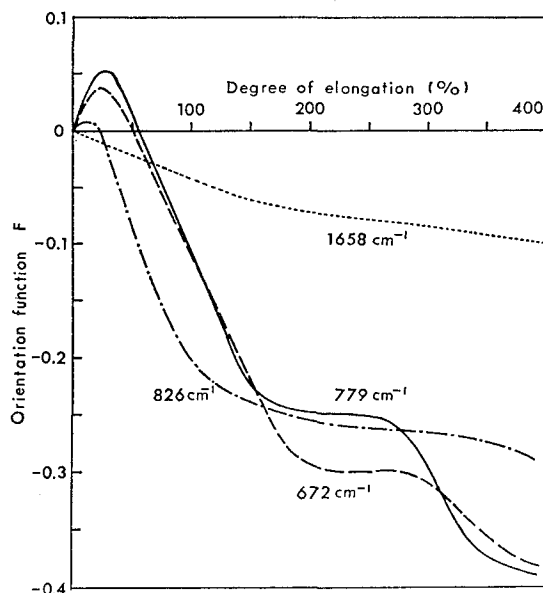


Fig. 2. Change in the orientation functions for the four absorption bands of polychloroprene film during continuous elongation at 25 %/min.

The sample films were continuously stretched up to 400 % elongation at the constant rate of 25 %/min. Simultaneous measurements were made of the infrared dichroism and tensile force. Figure 2 gives changes in the orientation functions for the four absorption bands during the course of the continuous elongation. It is seen that the orientation functions of the two crystalline-sensitive bands at 672 and 779 cm^{-1} change in a similar manner each other, that is, they increase at first until maxima at about 25 % elongation, and then decrease very rapidly to about 150 % elongation changing their signs from positive to negative. After passing through the flat part between about 150 and 300 % elongation,

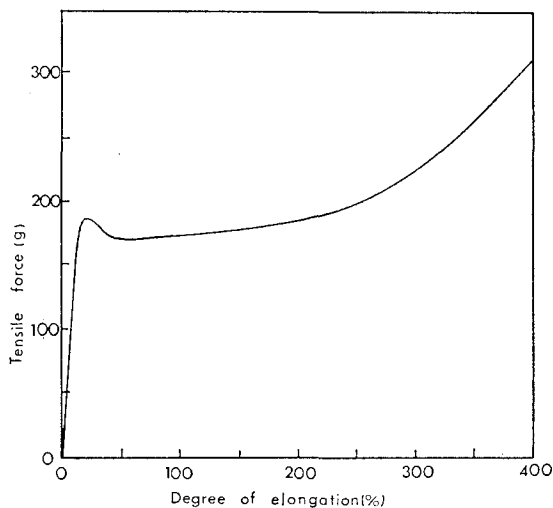


Fig. 3. Stress-strain curve of polychloroprene film continuously stretched at 25 %/min.

they decrease rapidly again. For the band at 826 cm^{-1} , the similar change but somewhat diffused is observed. This is interpreted by the overlap of the amorphous and crystalline-sensitive bands mentioned above, since the orientation function for the amorphous band decreases smoothly as can be seen from the curve for the 1658 cm^{-1} band in Fig. 2. Fig. 3 represents the stress-strain curve obtained at the same time as the dichroic measurements just mentioned. The tensile force increases almost linearly first and then come to the yield point at about 25 % elongation. Above this point it increases slowly up to about 200 % elongation and rapidly thereafter. In order to know the change in crystallinity during the continuous elongation, the A/d value for the crystalline-sensitive band at 779 cm^{-1} are plotted against the degree of elongation in Fig. 4. It is apparent that the degree of crystallinity begins to decrease at about 25 % elongation and has its minimum at about 150 % elongation.

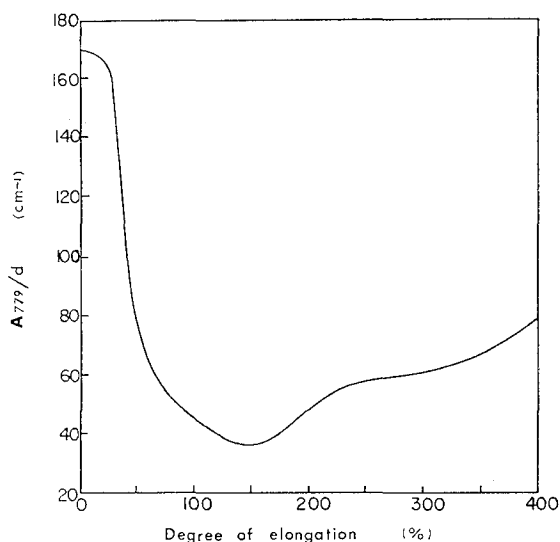


Fig. 4. Change in A_{779}/d value of polychloroprene film during continuous elongation at 25 %/min.

It should be noticed that, in Figs. 2, 3, and 4, there appear distinctive points at the same degree of elongation of 25 %. Those are the maximum of the orientation function for the crystalline-sensitive bands in Fig. 2, the yield point in the stress-strain curve (Fig. 3), and the beginning of sharp decrease of crystallinity in Fig. 4. Since, as is described above, the crystalline-sensitive bands at 779 and 672 cm^{-1} have their transition moments parallel to the ab -plane of the crystal, the increase of the orientation function for these bands at the beginning of the elongation suggests that the crystallites are oriented so that the a - or b -axis tends to be directed in the stretching direction. In other words, the molecular chains in the crystallites tend to make perpendicular orientation to the stretching direction. The sharp decrease of the orientation functions between about 25 and 150 % elongation suggests that the molecular chains are drawn out from the crystallites and are oriented to put their chain axes parallel to the stretching direction.

If the molecular chains are folded in the crystal as in the case of polyethylene, this process means the unfolding of the molecular chains from the crystallites. In this process, the crystallites should be degraded and the crystallinity should be reduced. This is shown to be the case in Fig. 4. It is therefore likely that the yield point at 25 % elongation in the stress-strain curve (Fig. 3) corresponds to the point of transition from the crystal orientation to the molecular orientation which accompanies the degradation of the crystallites and drawing out of the molecular chain from the crystallites.

The region of elongation more than 150 % is thought to be that of recrystallization of the oriented molecular chains, because the A/d value for the 779 cm^{-1} band increases gradually (Fig. 4). Until about 300 % elongation of this region the recrystallization takes place without appreciable orientation as is seen in Fig. 2. Above this elongation, however, the orientation of the crystallites occurs predominantly, so that the chain axes in the crystallites tend to make a perfect parallel orientation to the stretching direction (Fig. 2).

3. Stress relaxation

The simultaneous measurements of stress relaxation and infrared dichroic change were made at 400 % elongation and at fixed wavenumbers of the four absorption band maxima mentioned above. As in the case of natural rubber⁽¹⁾, when the sample is rapidly stretched and then held at the constant elongation, the pen of the infrared spectrometer instantly goes up or down by T_0 from the initial position of the unstretched sample, depending upon the parallel and perpendicular dichroism of the absorption bands and then gradually moves in the same direction attaining to a constant value. The instantaneous changes F_0 in the orientation function for the four absorption bands are calculated from T_0 by using eq. (1), and the ratios F/F_0 are plotted against time in Fig. 5. It is seen

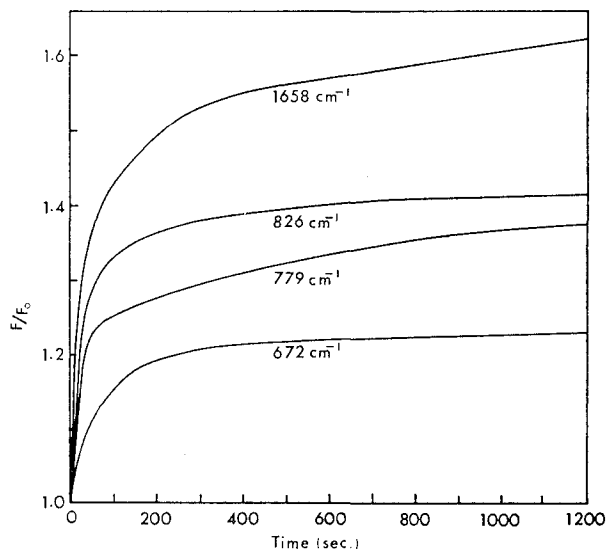


Fig. 5. Change in F/F_0 value for the four absorption bands of polychloroprene film during stress relaxation at 40 % elongation.

that the ratios F/F_0 increase rapidly first and then gradually until constant values. Although the F/F_0 value for the crystalline-insensitive band at 1658 cm^{-1} is slightly larger than that for the crystalline-sensitive bands at 779 and 672 cm^{-1} , the difference between these values is not so definite as that in the case of natural rubber⁽¹⁾. This fact suggests that in polychloroprene sample the orientation in the crystalline phase is almost the same as that in the amorphous phase. It makes a contrast with the previous results for vulcanized natural rubber⁽¹⁾, where the orientation of the crystalline phase was completed almost immediately after elongation, while in the amorphous phase the molecular chains were oriented gradually during the course of stress relaxation. This may be partly due to the fact that room temperature at which all the experiments are carried out is below the melting point ($50 \pm 5^\circ\text{C}^{(6)}$) polychloroprene and above that ($10 \pm 10^\circ\text{C}^{(12)}$) of natural rubber. Since no close correspondence is seen between F/F_0 vs. time curve (Fig. 5) and stress relaxation curve (Fig. 6), it is so far difficult to interpret the mechanism of the stress relaxation in terms of the amorphous and crystalline orientation.

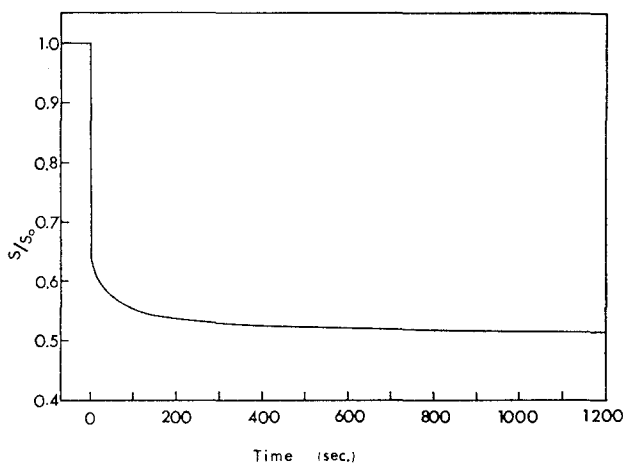


Fig. 6. Stress relaxation curve of polychloroprene film stretched by 400 %.

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